

gested by Phillips,¹⁷ we find the size of the required correction to be (1 ± 4) , (19 ± 1) , and $(125\pm 4)\times 10^{-6}$ for K, Rb, and Cs, respectively. These corrections are in reasonable agreement with the estimates made by Phillips,¹⁷ although the Cs correction is somewhat higher than expected.

Previous experiments relating to the K, Rb, and Cs g factors have been done by Franken and Koenig¹⁸ and by Kusch and Taub.¹⁹ The results are

$$\begin{aligned}(g_{\text{K}}/g_{\text{H}})_{\text{F+K}} &= 1 + (16\pm 4)\times 10^{-6}, \\ (g_{\text{Rb}}/g_{\text{Na}})_{\text{K+T}} &= 1 + (50\pm 10)\times 10^{-6}, \\ (g_{\text{Cs}}/g_{\text{Na}})_{\text{K+T}} &= 1 + (134\pm 7)\times 10^{-6}.\end{aligned}$$

Since the Margenau and Lambe corrections give $(g_{\text{Na}}/g_{\text{H}}) = 1 + (4.8)\times 10^{-6}$ and the effect of excited core states is expected to be even smaller for sodium than

for potassium, we find

$$\begin{aligned}(g_{\text{Rb}}/g_{\text{H}})_{\text{K+T}} &= 1 + (55\pm 10)\times 10^{-6}, \\ (g_{\text{Cs}}/g_{\text{H}})_{\text{K+T}} &= 1 + (139\pm 7)\times 10^{-6}.\end{aligned}$$

Looked at in this way, the previous results were somewhat high for potassium and rubidium but were in agreement with recent results for cesium.

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¹⁷ M. Phillips, Phys. Rev. **88**, 202 (1952).

¹⁸ P. Franken and S. Koenig, Phys. Rev. **88**, 199 (1952).

¹⁹ P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

Emission Spectrum of ZnIn

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The spectrum of ZnIn shows bands which can be analyzed into four systems. Two narrow systems at $\lambda 4102$ and $\lambda 4511$ appeared continuous. Systems at $\lambda 5308$ ($B-A$) and $\lambda 5625$ ($D-C$) were photographed with a dispersion of $5 \text{ \AA}/\text{mm}$. A possible vibrational analysis has been made for them. These systems exhibit an isotope effect which shows ZnIn as the emitter. Probable electronic states are ${}^2\Pi - {}^2\Sigma$ for $\lambda 5308$ and ${}^2\Sigma - {}^2\Sigma$ for $\lambda 5625$. Constants obtained are as follows: for $B^2\Pi_{1/2} - A^2\Sigma$ subsystem, $\nu_e = 18810.8$, $\omega_e' = 201.2$, $\omega_e'x_e' = 0.6$, $\omega_e'' = 146.7$, $\omega_e''x_e'' = 0.7$; for $B^2\Pi_{3/2} - A^2\Sigma$ subsystem, $\nu_e = 18831.2$, $\omega_e' = 193.9$, $\omega_e'x_e' = 0.6$ and for $D-C$ system, $\nu_e = 17732.0$, $\omega_e' = 107.0$, $\omega_e'x_e' = 1.0$, $\omega_e'' = 56.1$, and $\omega_e''x_e'' = 0.1$.

1. INTRODUCTION

THE band spectrum of HgTl and HgIn have been studied by Winans, Pearce, Davis, Leitzke, and Purbrick.¹⁻³ Both of these molecules show band systems of two general types. One type is a short-wavelength range system on the long-wavelength side of Tl or In lines. The other type is a group of bands with sharp heads showing overlapping sequences. An attempt to observe spectra from similar molecules has led to the present study of the spectrum of ZnIn.

2. EXPERIMENTAL ARRANGEMENTS

Spectra were excited in a quartz tube of length about 5 cm and diameter 1 cm, with a flat window on one end. Tubes were degassed at less than 10^{-6} mm and zinc and

indium inserted by distillation. Tubes were usually sealed off containing argon at about 3 mm pressure. Argon, however, is not necessary to obtain the ZnIn spectrum.

A 200-W oscillator at a frequency of about 100 Mc/sec served for excitation with external electrodes. The heat necessary to maintain the required pressures of indium and zinc was provided by a blow torch. Spectra were photographed with Bausch and Lomb medium quartz and quartz Littrow spectrographs and with a 3.4-m Jaco Ebert Plane grating spectrograph of dispersion $5 \text{ \AA}/\text{mm}$ in the first order. Exposures of 5 h with Kodak IIF plates were sufficient.

3. RESULTS

Fig. 1(a) shows the band systems photographed with the medium quartz spectrograph. The spectrum shows two continuous bands near the In lines $\lambda 4102$ and $\lambda 4511$ and two groups of bands with intensity maxima at

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¹ J. G. Winans and W. J. Pearce, Phys. Rev. **74**, 1262 (1948).

² J. G. Winans, Davis, and Leitzke, Phys. Rev. **51**, 70 (1940).

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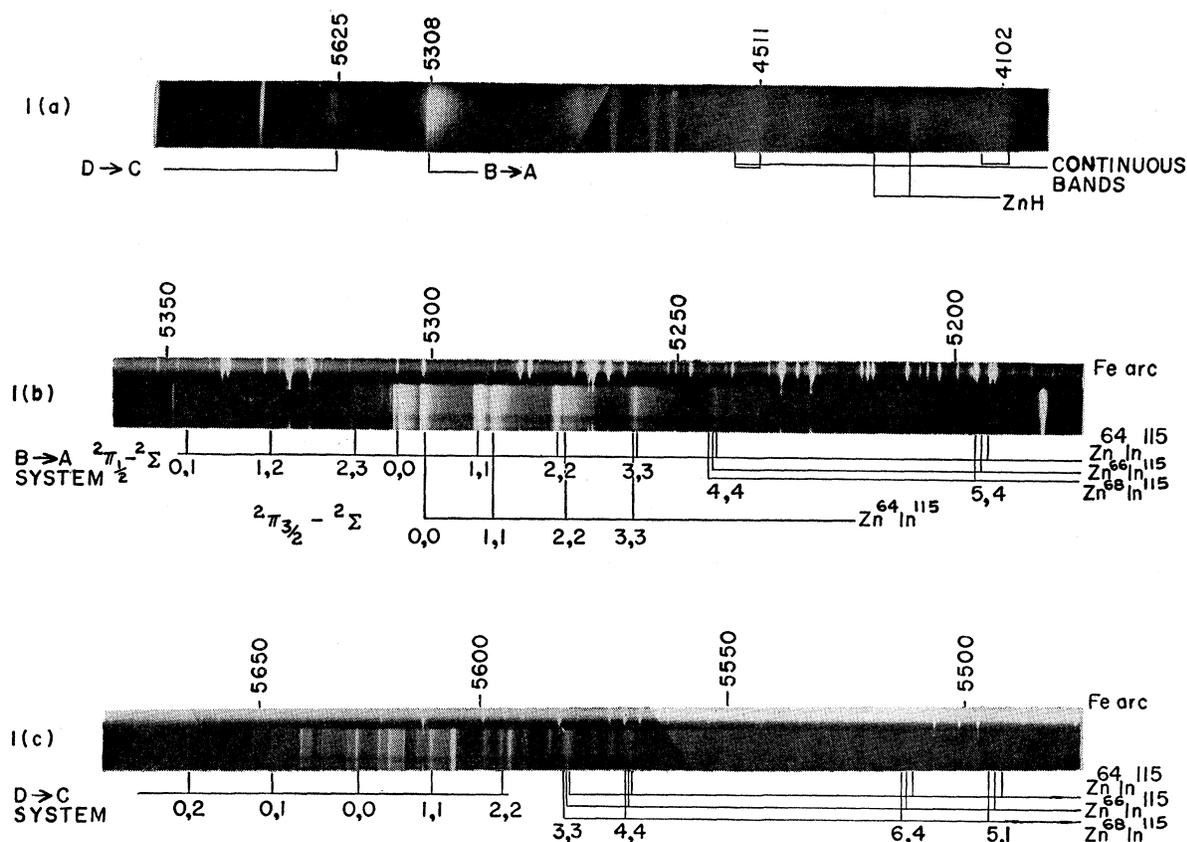


FIG. 1. The band spectrum of ZnIn.

$\lambda 5308$ and $\lambda 5625$. The bands at $\lambda 5308$ have been designated as the $B-A$ system and those at $\lambda 5625$ as the $D-C$ system. Figure 1(b) shows the $B-A$ system and Fig. 1(c) the $D-C$ system photographed with $5 \text{ \AA}/\text{mm}$ dispersion. The wave numbers at the heads of the bands for the $B-A$ and $D-C$ systems are given in Table I.

The continuous bands near the In lines at $\lambda 4511$ and $\lambda 4102$ extend with nearly uniform intensity from the lines to long-wavelength limits at $\lambda 4539$ and $\lambda 4134$, respectively.

4. INTERPRETATION AND ANALYSIS

The molecule ZnIn in the ground state is composed of a closed-shell atom ($\text{Zn } d^{10}s^2$) and an atom with an external p electron ($\text{In } s^2p$). Since the outer two electrons in Zn have the same character as the electrons for He in the ground state, there should be no binding or only a very weak polarization binding between In and Zn in the ground state. If the In is excited, the binding should still be very weak but might be somewhat stronger due to increased polarization of the Zn atom by the excited In atom. The spectrum should consist of a set of bands or a continuum located close to In atomic

lines. The continuous bands near the In lines $\lambda 4511$ and $\lambda 4102$ can be interpreted as band systems of this type.

If the Zn atom is excited, there can be binding between Zn and In due to the exchange of the excited electron of Zn with the p electron of In. This should provide a spectrum showing normal-type band systems. The band systems with maxima at $\lambda 5308$ and $\lambda 5625$ are considered to be band systems of this type.

Potential curves which account for the continuous bands are shown in Fig. 2. The upper state formed from excited indium and unexcited zinc is considered to have a slight minimum, while the two lower states are considered to have no minima as assumed also by Purbrick for the corresponding bands of HgIn. The long-wavelength limits at $\lambda 4134$ and $\lambda 4539$ correspond to the transitions AC and AB in Fig. 2. The dissociation energy of the upper state thus equals the energy difference between the long wave limits and the In lines. The average value for this energy difference is 162 cm^{-1} .

$B-A$ System ($\lambda 5308$)

The bands of this system appear double headed and are clearly degraded towards shorter wavelengths. The double heads can be considered as P and Q heads. The

TABLE I. Band heads of $D-C$ and $B-A$ systems.

v', v''	Band heads (cm^{-1})			Intensity of $\text{Zn}^{64}\text{In}^{115}$	Observed-Calculated for $\text{Zn}^{64}\text{In}^{115}$
	$\text{Zn}^{64}\text{In}^{115}$	$\text{Zn}^{66}\text{In}^{115}$	$\text{Zn}^{68}\text{In}^{115}$		
$D-C$ system (${}^2\Sigma-{}^2\Sigma$)					
2, 6	17 631.4			2	-1.4
0, 2	17 645.1			3	+0.5
3, 7	17 677.5			2	-1.8
2, 5	17 688.6			4	+0.9
0, 1	17 700.7			4	-0.6
4, 8	17 720.3			6	-3.3
3, 6	17 734.5			4	+0.7
2, 4	17 743.6			2	+0.8
1, 2	17 751.4			5	+0.8
0, 0	17 757.2			8	0.0
4, 7	17 778.9			7	+0.6
2, 3	17 799.0	17 798.3	17 797.6	5	+0.9
1, 1	17 807.7	17 806.8	17 805.5	7	+1.6
5, 8	17 820.8				+0.2
4, 6	17 833.9			1	+1.1
3, 4	17 843.8	17 842.7	17 841.5	4	0.0
2, 2	17 854.8	17 853.5	17 852.5	5	+1.2
1, 0	17 861.2			6	-1.0
6, 9	17 871.5	17 870.1	17 868.6	4	+0.2
4, 5	17 887.8	17 886.5	17 885.0	5	+0.1
3, 3	17 899.9	17 898.6	17 896.5	6	-0.8
6, 8	17 918.7	17 916.7	17 915.1	3	+3.1
5, 6	17 930.3	17 928.5	17 926.9	4	+0.5
4, 4	17 943.1	17 941.1	17 939.2	5	+0.3
2, 0	17 963.9	17 961.7	17 959.5	3	-1.3
6, 7	17 972.9	17 970.8	17 968.6	2	+2.6
5, 5	17 984.5			1	-0.2
3, 1	18 007.7	18 005.2	18 003.5	1	-2.6
5, 3	18 097.1	18 093.1	18 089.7	1	+2.0
4, 1	18 109.7	18 106.1	18 102.2	1	+0.6
6, 4	18 139.2	18 135.2	18 131.1	2	+4.4
5, 1	18 201.8	18 197.4	18 192.9	2	-4.5
6, 2	18 246.9			2	+1.3
$B-A$ system (${}^2\Pi_{1/2}-{}^2\Sigma$)					
0, 1	18 693.2Q			2	+0.5
1, 2	18 748.4Q			3	-0.3
2, 3	18 805.1Q			3	0.0
0, 0	18 834.2P				
0, 0	18 838.0Q			10	0.0
1, 1	18 889.8P				
1, 1	18 892.3Q			9	-0.4
2, 2	18 945.5P				
	18 947.2Q			8	-0.4
3, 3	19 000.8P				
3, 3	19 002.3Q			6	-0.3
4, 4	19 057.0P	19 054.4P	19 052.0P		
4, 4	19 058.1Q	19 055.6Q	19 053.3Q	5	+0.2
5, 5	19 114.2Q			3	+0.8
3, 2	19 144.3Q			4	-0.8
4, 3	19 198.4Q			4	-0.6
5, 4	19 250.8P	19 246.5P	19 242.6		
5, 4	19 252.5Q	19 248.7Q	19 244.2	3	-0.6
6, 5	19 307.7Q			3	+0.2
$B-A$ system (${}^2\Pi_{3/2}-{}^2\Sigma$)					
0, 0	18 852.7P				
	18 854.8Q			9	0.0
1, 1	18 900.6P				
	18 902.6Q			8	+0.2
2, 2	18 950.8Q			7	-3.4
3, 3	18 996.9P				
	18 998.7Q			5	-1.4

heads have the appearance of a v' progression, but the decrease in P, Q separation from band to band indicate that they form instead a sequence. The P, Q head separation is given by

$$\Delta\nu = -(B' + B'')^2 / 4(B' - B'')$$

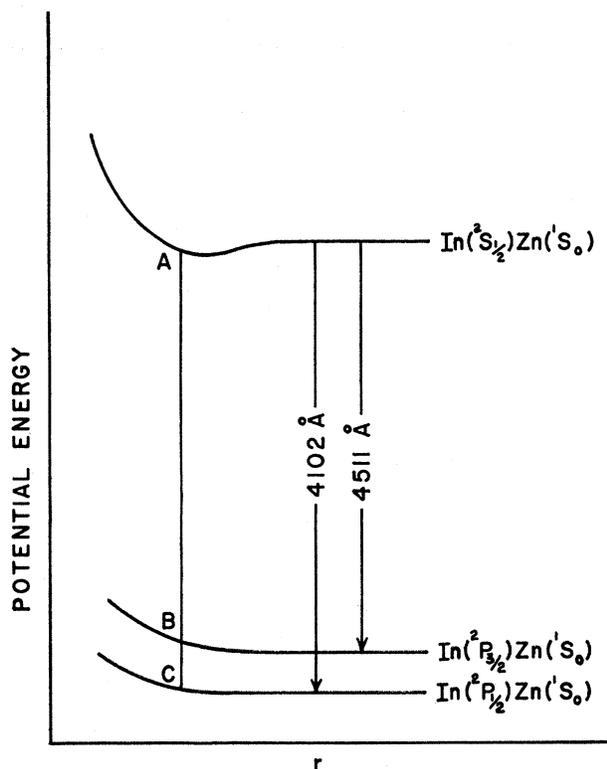


FIG. 2. Potential curves and dissociation products of the continuous bands.

For a v' progression in a violet degraded band system ($B' > B''$), B'' is constant and B' decreases with v . This will decrease $(B' - B'')$ and increase $\Delta\nu$ as v increases. If spectra show that $\Delta\nu$ decreases with increase in v , the group cannot represent a progression. The bands in question must therefore form a sequence. In addition, interpretation as a sequence enables the weak bands on the low-frequency side to be fitted into the analysis. The bands can be analyzed into two subsystems of a ${}^2\Pi-{}^2\Sigma$ transition, the assignment being in accordance with the double-headed nature of the bands. The subsystem ${}^2\Pi_{1/2}-{}^2\Sigma$ which lies on the low-frequency side shows three sequences. The following vibrational quantum formula represents the Q heads of $\text{Zn}^{64}\text{In}^{115}$ of this subsystem.

$$\nu = 18810.8 + 201.2(v' + \frac{1}{2}) - 0.6(v' + \frac{1}{2})^2 - 146.7(v'' + \frac{1}{2}) + 0.7(v'' + \frac{1}{2})^2.$$

The other component system ${}^2\Pi_{3/2}-{}^2\Sigma$ shows only one sequence of bands with $\Delta v = 0$, from which it is not possible to derive the vibrational constants. However, assuming the lower state to be $A^2\Sigma$, the following constants were obtained for the $B^2\Pi_{3/2}-A^2\Sigma$ subsystem; $\nu_e = 18831.2K$, $\omega_e' = 193.9K$, $\omega_e'x_e' = 0.6$. The ${}^2\Pi$ separation was obtained from the wave number difference between the two system origins (18831.2-18810.8) as 20.4K. This small separation for rather a heavy

TABLE II. Deslandres table of the $B-A$ system^a (${}^2\Pi_{1/2}-{}^2\Sigma$).

$v'' \backslash v'$	0	1	2	3	4	5
0	10	144.8	2 199.1			
1		9	143.9	3 198.8		
2			8	141.8	3	
3			197.1	4	196.9	
4				142.0	6 196.1	
5					4	140.3
6					5 194.4	3
						138.3
						3
						192.5
						3

^a Intensities and vibrational quantum refer to the Q heads.

molecule shows that the ${}^2\Pi$ state belongs to a case intermediate between (a) and (b). Table I shows the vibrational assignments and wave numbers of the band heads. Deslandres arrangement of the subsystem ${}^2\Pi_{1/2}-{}^2\Sigma$ is displayed in Table II.

$D-C$ System

The bands of this system lie in the region $\lambda 5670-\lambda 5470$ and most of the bands are degraded towards the violet. The general appearance of this system is more complex than that of the $B-A$ system. However, two clearly marked sequences have been identified. The short-wavelength bands of this system showed clear triple heads. These were identified as isotopic bands due to Zn^{64} , Zn^{66} , and Zn^{68} . From the measurements of the isotopic shifts the position for zero isotope shift was determined. This showed that the sequences observed were the $\Delta v=0$ and $\Delta v=-1$ sequences. The remainder of the bands fitted into the scheme. The following formula was derived to represent the heads of the most abundant molecule $Zn^{64}In^{115}$.

$$\nu = 17732.0 + 107.0(v' + \frac{1}{2}) - 1.0(v' + \frac{1}{2})^2 - 56.1(v'' + \frac{1}{2}) + 0.1(v'' + \frac{1}{2})^2.$$

The Deslandres arrangement of this system showing estimated intensities and observed separations of the bands is given in Table III. Figure 1(c) shows assignments for some of these bands. Some bands in this system have two heads, one on each side. The second head may be due to the reversal of the R branch for high J values, which can occur if $D'-D''$ has the same sign as $B'-B''$ (Herzberg 1950).⁴ An overlapping with a red degraded system may also account for the two heads of some bands. The absence of Q heads in these bands indicate that the $D-C$ system may arise from a ${}^2\Sigma-{}^2\Sigma$ transition.

Isotope Effect

The three Zn isotopes Zn^{64} , Zn^{66} , and Zn^{68} have an abundance ratio of 51:27:17. The triple heads of the bands of $D-C$ and $B-A$ were identified as due to the molecules $Zn^{64}In^{115}$, $Zn^{66}In^{115}$, and $Zn^{68}In^{115}$. The relative intensities of these bands are consistent with the abundance ratio of Zn isotopes. The ratio of the reduced mass of the most abundant molecule to that of the isotopic molecule (ρ) for $Zn^{64}In^{115}$ and $Zn^{66}In^{115}$ is 0.990218 and for $Zn^{64}In^{115}$ and $Zn^{68}In^{115}$ is 0.980922. The expected isotope shifts were calculated using the

TABLE III. Deslandres table of the $D-C$ system (estimated intensities and observed differences).

$v'' \backslash v'$	0	1	2	3	4	5	6	7	8	9
0	8	56.5	4	55.6	3					
	104.0		107.0		106.3					
1	6	53.5		56.3	5					
	102.7			103.6						
2	3		5	55.8	5	55.4	2	55.0	4	57.2
					100.9		100.3		100.6	
3		1			6	56.1	4	54.6	4	54.7
		102.0					99.3	98.6	99.4	57.0
4		1					5	55.3	5	53.9
									1	55.0
5									1	96.4
					1					4
6										7
									2	54.2
									3	97.9
										1
										47.2
										4

⁴ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

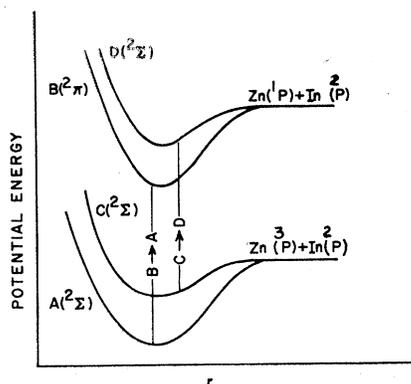


FIG. 3. Possible electronic states and dissociation products for $B-A$ and $D-C$ systems.

equation $\Delta\nu = (\rho - 1)\nu_v$, where ν_v is the wave number separation between system origin and the band head. The calculated and observed isotope shifts for the bands of the two systems are shown in Table IV. Figure 1(b)

TABLE IV. Isotope effect.

v', v''	Obs. Shift for $Zn^{64}In^{115}$ and $Zn^{66}In^{115}$	Cal. for $Zn^{64}In^{115}$ and $Zn^{66}In^{115}$	Obs. Shift for $Zn^{64}In^{115}$ and $Zn^{68}In^{115}$	Cal. Shift for $Zn^{64}In^{115}$ and $Zn^{68}In^{115}$
$D-C$ system				
2, 3	0.7	0.7	1.4	1.3
1, 1	0.9	0.7	1.2	1.3
3, 4	1.1	1.1	2.3	2.1
2, 2	1.3	1.2	2.3	2.4
6, 9	1.4	1.4	2.9	2.7
4, 5	1.3	1.5	2.8	3.0
3, 3	1.3	1.6	3.4	3.2
6, 8	2.0	1.8	3.6	3.6
5, 6	1.8	1.9	3.4	3.8
4, 4	2.0	2.1	3.9	4.0
2, 0	2.2	2.3	4.4	4.4
6, 7	2.1	2.4	4.3	4.6
3, 1	2.5	2.7	4.2	5.3
5, 3	4.0	3.6	7.4	7.0
4, 1	3.6	3.7	7.5	7.2
6, 4	4.0	4.0	8.1	7.8
7, 5	4.2	4.4	8.6	8.6
5, 1	4.4	4.6	8.9	8.9
$B-A$ system ^a				
4, 4	2.5	2.4	4.8	4.7
5, 4	3.8	4.3	8.3	8.4

^a Isotopic shifts correspond to the Q heads.

and 1(c) shows the classification of the heads of the isotopic molecules.

Discussion

Possible electronic states and dissociation products of the $B-A$ and $D-C$ systems are given in Fig. 3. The electronic states for these systems arise from excited zinc and unexcited indium atoms. The low-lying excited states of the Zn atom are 3P and 1P . The atomic states 3P of $Zn+^2P$ of In give the molecular states $\Sigma(3)$, $\Pi(2)$, and Δ , each with multiplicities 2 and 4, whereas 1P of $Zn+^2P$ of In gives $^2\Sigma$, $^2\Pi$, and $^2\Delta$. If we assume these dissociation products for the lower and upper states of both systems, the possibility of a quartet state as the lower can be eliminated because of the selection rule $\Delta S=0$. The $D-C$ system shows bands with single heads suggesting a $^2\Sigma-^2\Sigma$ transition. The $B-A$ system which shows strong Q heads that can be expected when $\Delta\Lambda = \pm 1$, probably represents a $^2\Pi-^2\Sigma$ transition. The lower (A, C) states of these systems may be considered as two $^2\Sigma$ states arising from $^3P+^2P$ and the upper (B, D) states as $^2\Pi$ and $^2\Sigma$ from the combination $^1P+^2P$. The vibrational constants of ZnIn molecule are summarized in Table V.

TABLE V. Vibrational constants of ZnIn.

State	T_e	ω_e	$\omega_e x_e$	Designation	Observed transitions ν_{00}
$D(^2\Sigma)$	$C+17\ 732.0$	107.0	1.0	$D-C$	17 757.2
$C(^2\Sigma)$	C	56.1	0.1		
$B(^2\Pi_{3/2})$	$A+18\ 831.2$	193.9	0.6	$B-A$	18 854.8
$B(^2\Pi_{1/2})$	$A+18\ 810.8$	201.2	0.6		18 838.0
$A(^2\Sigma)$	A	146.7	0.7		

To make sure that both Zn and In are necessary to obtain these bands, spectra were taken with one tube containing In alone and another tube containing Zn alone. Neither of these tubes showed the bands ascribed to ZnIn. The agreement of the calculated and observed isotope effect also shows that the carrier of the band spectrum is a ZnIn molecule.

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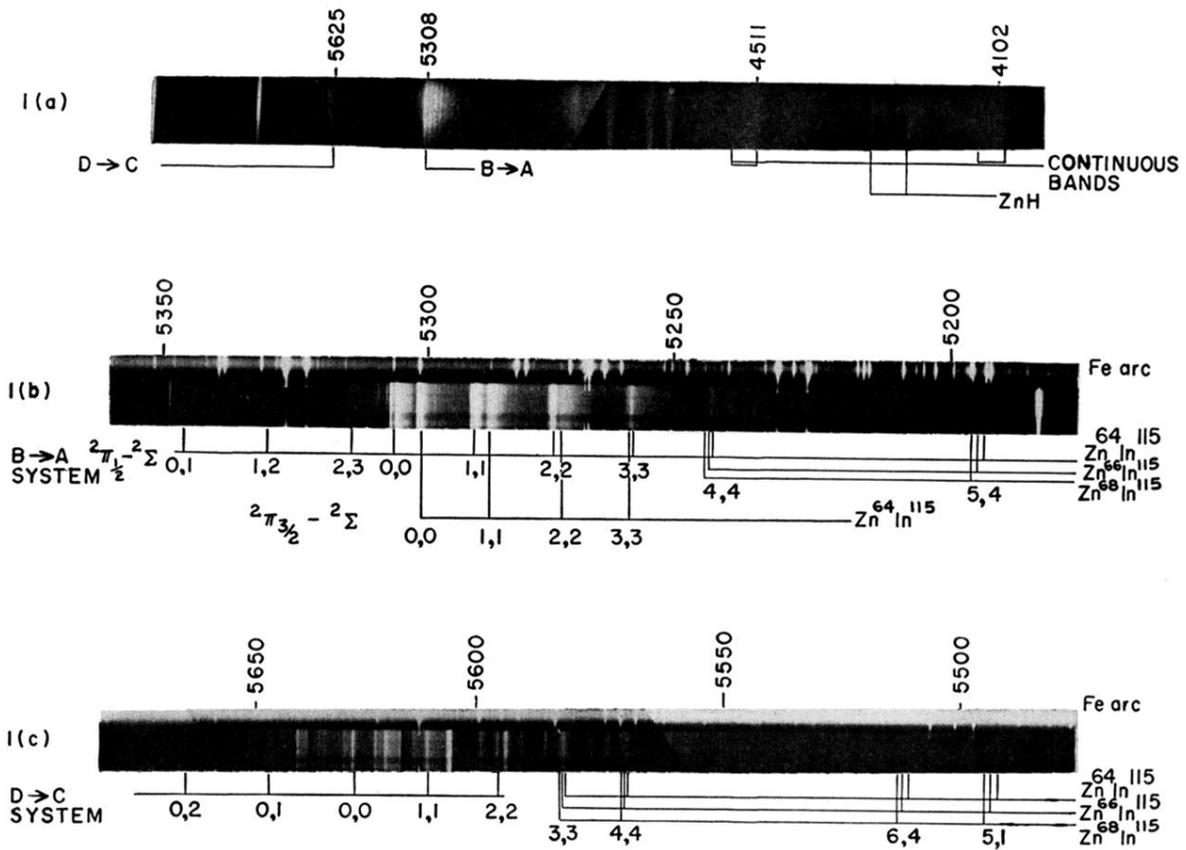


FIG. 1. The band spectrum of ZnIn.